CoSb$_3$-IrSb$_3$ Solid Solutions: Preparation and Characterization

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ABSTRACT

The binary antimonide compounds of the skutterudite family have a good potential for thermoelectric applications as recent results at the Jet Propulsion Laboratory (JPL) have shown [1-3]. However, the room temperature thermal conductivity of these materials is about 10 Wm^{-1}K^{-1} with an estimated 80°/0 contribution from the lattice. To achieve maximum ZT values, the lattice thermal conductivity needs to be lowered. Because the lattice thermal conductivity of solid solutions can substantially decrease due to the addition of point defect phonon scattering (all state of the art thermoelectric materials ate solid solutions), a study of the formation of solid solutions between the antimonide skutterudite compounds is of interest. The existence of CoP$_3$-CoAs$_3$ and CoAs$_3$-CoSb$_3$ solid solutions was already reported in the literature [4]. The preparation and characterization of both p-type and n-type CoSb$_3$-IrSb$_3$ solid solutions by several techniques is reviewed in this paper.   The homogeneity of the samples and the existence of solid solutions were investigated using mass density measurements, X-ray diffractometry, microprobe analysis and optical microscopy.   The thermal conductivity, the electrical resistivity, and the hall mobility were measured from 25 to 500°C. Experimental results showed that solid solutions were successful y formed in a wide range of compositions. Some immiscibility was observed but may be due to the preparation conditions. The changes in the thermoelectric properties indicated the influence of a strong point defect scattering, resulting in large decreases in Hall mobility and thermal conductivity. The potential for high ZT values in CoSb$_3$-IrSb$_3$ solid solutions is discussed.

1. INTRODUCTION

The search for new thermoelectric materials has recently focused at JPL on compounds with the skutterudite structure [1]. Experimental data obtained on both CoSb$_3$ and IrSb$_3$ have indicated that these materials combine interest ing electrical and thermal properties: high carrier mobility, low electrical resistivity, moderate Seebeck coefficient and moderate thermal conductivity [2,3,5]. Room temperature thermal conductivity of these materials is about 10 Wm^{-1}K^{-1} with an estimated 80°/0 contribution from the lattice [2,3].

At high temperatures (400-600"(), thermal conductivity values decrease to 5-6 Wm^{-1}K^{-1}. These values arc substantially higher than for state of the art thermoelectric materials as shown in Table 1. It should be noted that all state of the art thermoelectric materials are solid solutions, resulting in thermal conductivity values up to 9 times lower than that for

the original elemental or compound semiconductor. This is due to a sharp decrease in lattice thermal conductivity brought by the addition of point defect phonon scattering (atomic mass and atomic volume difference).

Table I: Lattice thermal conductivity λ_l for state of the art thermoelectric alloys [6], $IrSb_3$ and $CoSb_3$ [2,3].

State of the art material	λ_l ($Wm^{-1}K^{-1}$)	Temperature (K)
$Bi_{0.85}Sb_{0.15}$	2.73	100
$(Bi_2Te_3)_{0.25}(Sb_2Te_3)_{0.75}$	1.05	300
$(PbTe)_{0.6}(PbSe)_{0.4}$	1.11	300
$(InSb)_{0.7}(GaSb)_{0.3}$	4.88	300
$Si_{0.8}Ge_{0.2}$	6.02	300
$CoSb_3$	8.91	300
$IrSb_3$	9.83	300

A similar approach was applied to the reduction of the lattice thermal conductivity of antimonide skutterudite compounds by studying the possible formation of solid solutions. The existence of CoP_3-$CoAs_3$ and $CoAs_3$-$CoSb_3$ solid solutions has already been reported in the literature [4]. No quasibinary alloying behavior was expected due to the relatively large difference in lattice parameters (2.3%) and the incongruent melting character of the compounds (peritectic decomposition temperature of 1141 "C and $876^\circ C$ for $IrSb_3$ and $CoSb_3$ respectively). 110WCVCI, a wide range of compositions forming solid solutions [7] could still exist and the preparation of both p-type and n-type $CoSb_3$-$IrSb_3$ solid solutions by different powder metallurgy techniques was investigated.

2. SAMPLE PREPARATION

Previous attempts at growing $IrSb_3$ from a Sb-rich melt have always resulted in multiphase samples containing inclusions of Sb. This is due to the peritectic plateau of $IrSb_3$ extending up to 97 at.% Sb [8] and as a consequence only a very narrow range of compositions (with steep temperature variations) is available for crystal growth. $CoSb_3$ has been successfully prepared from an Sb-rich melt because the peritectic plateau only extends up to 92 at.% Sb and temperature variations arc smaller [9].

Preparation of $Co_{1-x}Ir_xSb_3$ compositions from the melt would be very difficult to control considering the lack of knowledge of the ternary phase diagram as well as the narrow range of Sb-rich compositions possible. Mechanical alloying of the elemental powders was ruled out because excessive contamination by the vial material (stainless steel or tungsten carbide) was found after long milling periods of time (more than 1 hour).

Two different techniques were developed, based on results obtained on both $CoSb_3$ and $IrSb_3$: hot-pressing of reacted powders (HP) and liquid-solid phase sintering of elemental powders (1. S1%). Samples prepared by these methods always showed p-type conductivity. N-type samples have also been obtained by adding suitable dopants in elemental form to the mix of Co, Ir and Sb. Results on doping studies and optimization of n-type and p-type $Co_{1-x}Ir_xSb_3$ solid solutions will be published later.

2.1 Hot-pressing:

The elemental powders (minimum of 99.9% purity) in amounts close to stoichiometric ratios were placed in a glassy carbon crucible, sealed into quartz ampoules under 10^{-5} Tort vacuum and reacted by solid state interdiffusion at 600°C. It has been found previously that very short times and low temperatures were suitable for preparing fully reacted $IrSb_3$ powders from the elemental constituents. For mixed Co, Ir and Sb compositions, a reaction time of 24 hours was found sufficient for the synthesis of a partially alloyed powder. This method allows preparation of large quantities in a relative] y contaminant ion-free environment.

The pre-reacted powders were then hot-pressed at 800°C for 2 hours in graphite dies of 6,35 mm ID at a pressure of 15000 psi. An "Astro" hot-pressing furnace with a constant flow of argon was used. Compact cylindrical pellets 6,4 mm in diameter and 5 to 8mm long were obtained by this process. To ensure a good homogeneity in composition, the hot-pressed samples were subsequently annealed at 800°C for 800 hours under vacuum in sealed quartz ampoules.

2.2 Liquid-solid phase sintering

Flat bottom 6.35mm ID quartz ampoules were carbon coated on the inside by cracking acetone and then annealed for a short period of time in vacuum. Elemental powders of Ir and Co were mixed and placed at the bottom of the ampoules. After Sb shots were added on top, the ampoules were sealed under vacuum (better than 10-5 Torr). Co, Ir and Sb elements were loaded in amounts close to stoichiometric ratios.

The ampoules were then heated up to 800°C for Co-rich compositions and up to 950°C for Ir-rich compositions. Temperatures were held for 24 hours. During the process, melted Sb diffused through metal powders and the liquid-solid phase sintering (LSPS) resulted in conical samples about 6.3 mm in diameter and up to 15 mm long

3. EXPERIMENTAL RESULTS

3.1 Microstructure

Samples prepared by the HP and LSPS processes were investigated using an optical microscope with and without light polarization or Nomarski contrast. Microprobe anal ysis (MPA) was performed on a JEOL JXA-733 electron superprobe operating at 20 kV of accelerating potential and 25x1 0^{-9} A of probe current. Pure elements were used as standards, and X-ray intensity measurements of peak and background were conducted by wavelength dispersive spectrometry. Mass densities were determined using the immersion technique. Because of the substantial porosity found, LSPS samples were held for at least 30 minutes in toluene before weighing to allow the liquid to penetrate the pores. A Siemens D-500 diffractometer produced diffractometry patterns at room temperature. Small additions of Pt powder were made to some samples as an internal standard.

Preparation of the samples by hot-pressing was found to be much more time consuming than the LSPS approach. However, results showed that HP samples were high quality

cylindrical samples with mass densities better than 98°/0 of the theoretical value (using a simple interpolation scheme) before annealing, whereas the LSPS samples were more porous and mass densities were in the 90-94% range of theoretical values (see Figure 1).

'Table 1l: Room temperature characterization of single phase homogeneous $CoSb_3$-$IrSb_3$ solid solution compositions

mol.% $IrSb_3$	prep.	a. Å	d g. cm^{-3}	d %theo	v_S m.s^{-1}	Θ_D K	p $10^{19}CnI$-3	μ_H m^{2}V^{-1}s^{-1}	P $\mu\Omega$m
100	HP	9.2533	9.19	98.3	2964	303	"2.42	1046	0.25
96	HP	-	9.12	98,2			0.59	293	3.60
92	HP		8,98	97.4			1.12	403	1.38
88	11P	9.2282	9.02	98,6	2.821	288	1.03	487	1.24
88	1 .SPS	-	8.63	94.3	2615	268	0.92	533	1.27
12	HP	9.0673	7.75	98.8			0.27	738	3.13
12	1.sl's	-					0.56	309	3,58
4	HP		7.61	98.7		-	0.214	494	
0	BG*	9.0385	7.63	100.0	2930	307	0.36	2062	. 3 : .

*Bridgman Growth

Experimental results on the room temperature characterization of single phase homogeneous solid solution compositions are reported in Table 1 I: preparation technique (prep.), lattice parameter a_0, mass density d, % of theoretical value, speed of sound vs, calculated Debye temperature Θ_D, p-type carrier concentration p, 1 Ian mobility μ_H and electrical resistivity ρ.
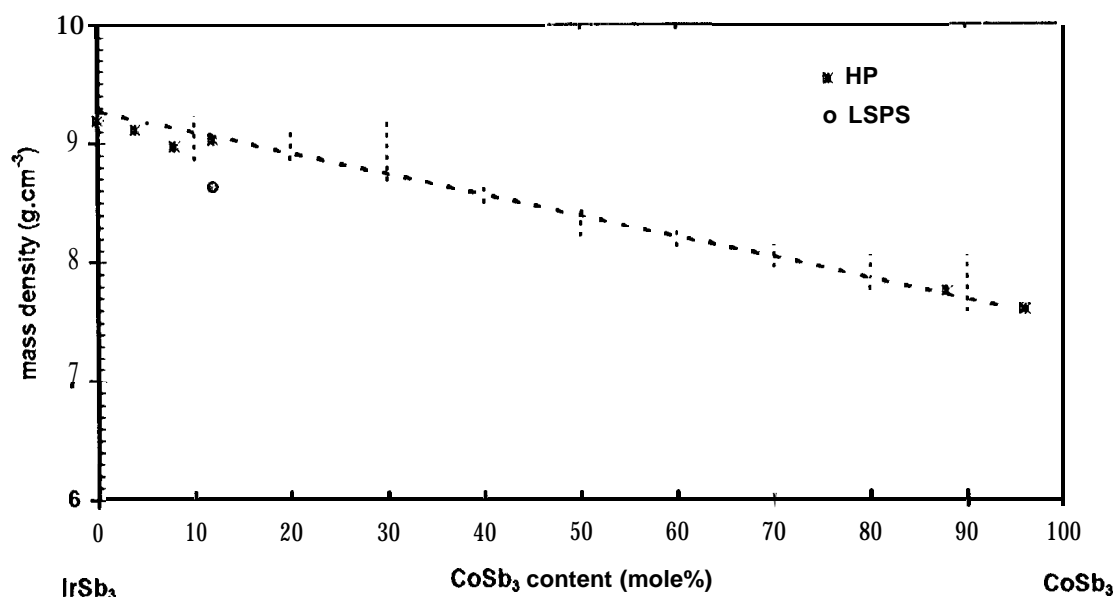
Figure 1: experimental mass densities for LSPS and HP $CoSb_3$-$IrSb_3$ samples. Dotted line corresponds to interpolated values between those obtained for $IrSb_3$ and $CoSb_3$.

MPA and X-ray analysis demonstrated that a partial solid solution range existed between the $CoSb_3$ and $IrSb_3$ compounds. Samples with compositions rich in Co required extensive annealing periods to achieve full homogeneity and eliminate traces of Ir-rich and Co-rich solid solution compositions (more than 96 mol% of any one compound). No unreacted Co, Ir or Sb, and no pure $CoSb_3$ or $IrSb_3$ were found by MPA.

Attempts to prepare compositions from 20 mol% up to 64 mol% $CoSb_3$ by hot pressing at the same conditions only resulted in multi-phase samples with Co-rich and Ir-rich compositions, indicating the possible existence of an immiscibility gap. This is illustrated in Figure 2 where variations in lattice parameter as a function of composition are reported.
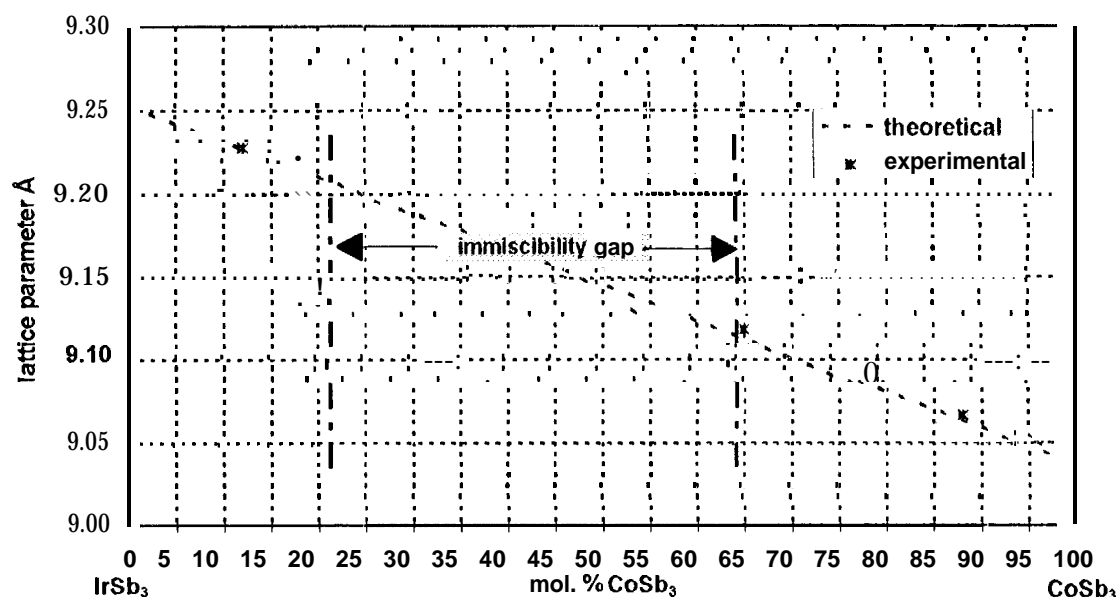

Figure 2: Experimental lattice parameter values determined for three HP $CoSb_3$-$IrSb_3$ samples. Dotted line corresponds to interpolation between $IrSb_3$ and $CoSb_3$ (Vegard's law). Possible immiscibility gap is highlighted.

The immiscibility region may have been caused by the relatively large lattice mismatch between $CoSb_3$ and $IrSb_3$. However, the hot-pressing preparation conditions involving solid state diffusion could also be a factor. Synthesis from an Sb melt (such as the LSPS method) could give different results.

3.2 Transport properties

The longitudinal and shear wave velocities of sound were measured on some samples using normal incidence transducers. The measurement technique used a frequency of 5 Mhz. Multiple reflections were used to increase the signal accuracy. Some results are shown in Table 11 and indicate that the calculated values of the Debye temperature of the solid solutions (270-290K) are reasonably close to those obtained for $CoSb_3$ (307K) and $IrSb_3$ (302K). Single phase samples were selected for Hall effect and van der Pauw electrical resistivity room temperature measurements. Some results for p-type

compositions are reported in Table 11.. The experimental Hall mobility values at $25^{\circ}C$ of three p-type $CoSb_3$-$IrSb_3$ solid solution samples are plotted on figure 3 as a function of carrier concentration. For a hole concentration of 10^{19} cm^{-3}, the mobility values of both $Co_{0.12}Ir_{0.88}Sb_3$ and $Co_{0.88}Ir_{0.12}Sb_3$ Compositions are about 40-50% of those achieved for $CoSb_3$ and $IrSb_3$.
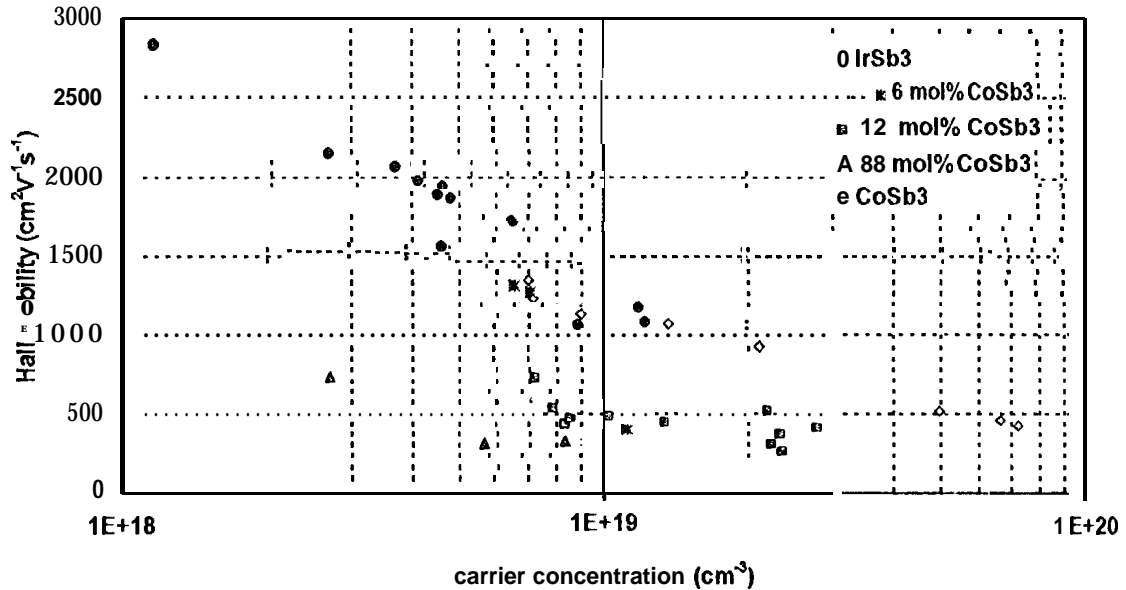
Figure 3: Room temperature Hall mobility values as a function of carrier concentration determined for three p-type $CoSb_3$-$IrSb_3$ solid solution compositions. Values obtained for p-type $IrSb_3$ and $CoSb_3$ samples are also plotted for comparison.
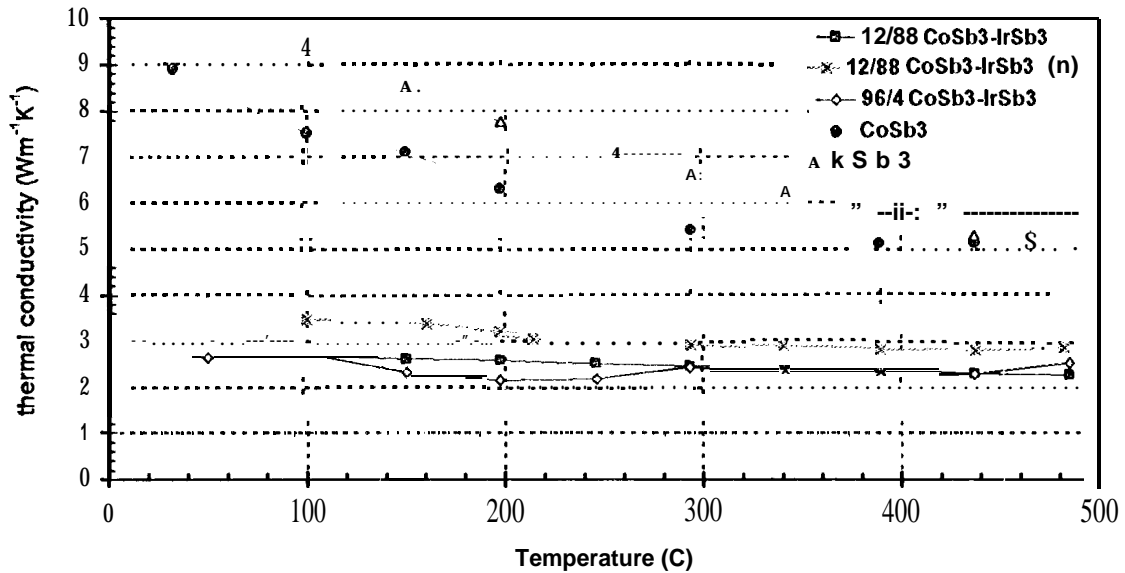
Figure 4: Experimental thermal conductivity values as a function of temperature determined for two p-type and one n-type $CoSb_3$-$IrSb_3$ solid solution compositions. Values obtained for p-type $IrSb_3$ and $CoSb_3$ samples are also plotted.

The decrease in mobility due to point defect scattering is clearly illustrated when comparing with results obtained on $IrSb_3$ and $CoSb_3$ samples. This difference becomes increasingly smaller for higher carrier concentrations as ionized impurity scattering of the carriers becomes more important.

Significant improvements in the figure of merit by forming solid solutions are possible only if the relative drop in lattice thermal conductivity is substantially larger than the corresponding decrease in carrier mobility. Two p-type and one n-type solid solution compositions were measured for thermal diffusivity and heat capacity from room temperature up to $500^\circ C$. Combining these two measurements, the calculated thermal conductivity y of these samples as a function of temperature is displayed in Figure 4. Results show a very large drop in thermal conductivity (70 to 75% lower) when compared to the values obtained for the two $CoSb_3$ and $IrSb_3$ compounds. These values of 2.5 to 3 W $.m^{-1}K^{-1}$ are comparable to results obtained for state of the art thermoelectric materials (see Table 1). The almost temperature independent variation of the thermal conductivity from 25 to 500"C (much different from the classical T^{-1} dependency) also indicated a "very strong point defect phonon scattering mechanism.
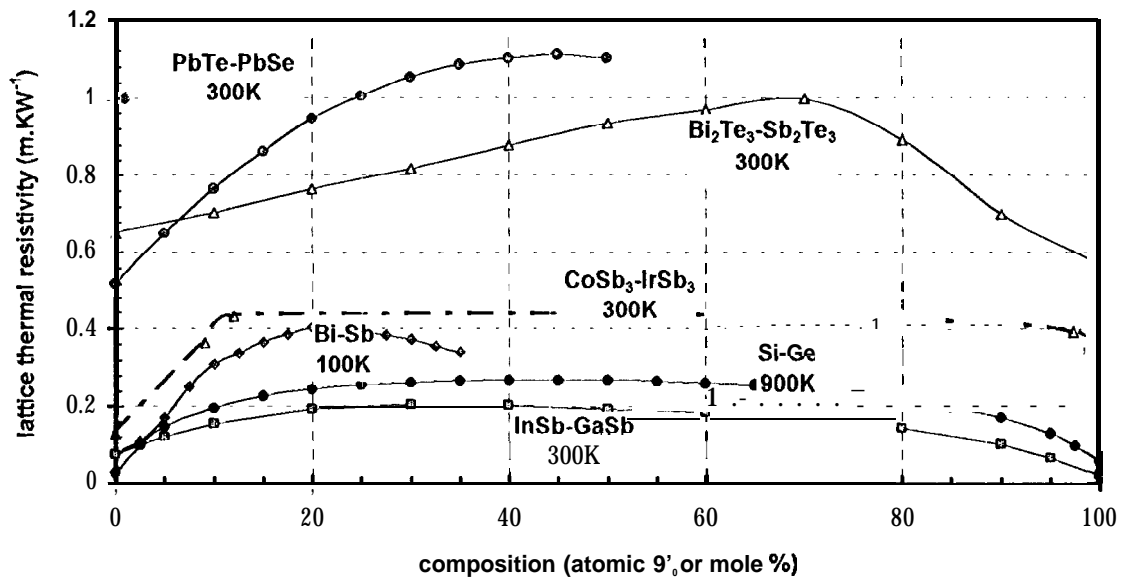
Figure 5: Lattice thermal resistivity values as a function of solid solution composition $CoSb_3-IrSb_3$ compositions. Values obtained for state of the art thermoelectric materials samples are also plotted.

Estimating the lattice contribution to the thermal conductivity using the Wiedemann-Franz law, Figure 5 compares the variations in lattice thermal resistivity as a function of the solid solution composition for several thermoelectric materials, The dotted line for $CoSb_3-IrSb_3$ compositions is only a tentative one as more data for various compositions needs to be collected.

3. CONCL1JS1ON

The existence of solid solutions in the $CoSb_3$-$IrSb_3$ system was demonstrated, Some partial immiscibility gap appears to be present and various preparation methods will be investigated to confirm it. Measurements of electrical and thermal transport properties showed the influence of strong point defect scattering mechanisms on the carrier mobility and thermal conductivity. Because of the relatively larger decrease in thermal conductivity over carrier mobility, higher thermoelectric figures of merit should be expected by forming solid solutions. Current studies are focusing on optimizing the composition and doping level of both p-type and n-type solid solutions.

ACKNOWLEDGMENTS

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